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<b>(54) Title:</b> NONLEADED FUEL COMPOSITION  <b>(57) Abstract</b>  Fuel compositions comprised of well-defined proportions of cyclopentadienyl manganese tricarbonyl antiknock compounds, solvents selected from the group consisting of C <sub>1</sub> to C <sub>6</sub> aliphatic alcohols and unleaded gasoline bases, possess improved long term hydrocarbon combustion emissions and technical enrichment characteristics. When methanol is used as the solvent it is desirable that a cosolvent selected from the group consisting of C <sub>2</sub> to C <sub>12</sub> aliphatic alcohols, C <sub>3</sub> to C <sub>12</sub> ketones and/or C <sub>2</sub> to C <sub>12</sub> ethers also be present in the fuel composition to assure phase stability.		

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NONLEADED FUEL COMPOSITIONBACKGROUND OF THE INVENTION1. Field of the Invention

05        This invention relates generally to novel fuel compositions for spark ignition internal combustion engines. More particularly, it relates to a novel additive combination for "nonleaded" gasoline compositions.

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## 2. Description of the Prior Art

05 The incorporation of various organo-metallic compounds as antiknock agents in fuels for high compression, spark ignited, internal combustion engines has been practiced for some time. The most common organo-metallic compound used for this purpose is tetraethyl lead ("TEL"). Generally these organo-metallic compounds have served well as antiknock agents. However, certain environmental hazards are now associated with the alkyl lead components of these compounds. This circumstance has precipitated a series of Environmental Protection Agency ("EPA") mandates aimed at completely phasing out leaded gasolines.

10 Many alternatives to these organo-metallic compounds also have been proposed and/or used. For example organomanganese compounds such as cyclomatic manganese tricarbonyls, particularly methylcyclopentadienyl manganese tricarbonyl ("MMT"), were once accepted alternatives to TEL. However, these compounds produced another set of environmental problems. Their use tends to steadily increase the amount of unoxidized and/or partially oxidized hydrocarbons. Fuels containing such organomanganese compounds gradually cause the emission of substantially higher levels of hydrocarbons than are permitted under law. Aggravating the air pollution problem, such organomanganese compounds, particularly MMT, when used at concentrations greater than about 1/16 per gram per gallon, are believed to be responsible for catalytic converter plugging. Accordingly, under Federal Law the use of MMT is currently banned in all unleaded gasolines.

30 It is well known in the art that many lower molecular weight aliphatic alcohols possess antiknock properties. They have been used as motor fuels in

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their own right and they have also been used as antiknock additives in both leaded and unleaded gasolines.

As might be expected, many attempts have been made to combine alkyl lead compounds, cyclomatic manganese tricarbonyls, and/or lower aliphatic alcohols with petroleum hydrocarbon products boiling within the gasoline range. Some combinations are the result of chemical compounding, while others represent noncompounded physical blends in various combinations. Certain combinations of these ingredients have been blended with or without the use of stabilizers. U.S. Patent 3,000,195 (the "195 patent") well summarizes the results of prior art efforts to physically blend TEL, MMT and certain lower aliphatic alcohol antiknock agents in gasoline without the aid of stabilizing agents. For example, the 195 patent points out that when lower aliphatic alcohols and TEL type compounds are present together in petroleum hydrocarbon gasolines, the antiknock effect achieved by the combination is substantially lower than would be expected in view of their known individual antiknock efficacies. This phenomena is commonly referred to as "negative lead susceptibilities". The 195 patent teaches that a positive synergism in the antiknock properties of leaded gasoline/alcohol fuel compositions can be obtained by adding a cyclomatic manganese tricarbonyl such as MMT to leaded gasoline compositions. However, at this time the technical advantages produced by such fuel compositions are being effectively negated by the phase out of lead containing antiknock additives.

Other investigations aimed at describing the physical properties of leaded gasoline/alcohol blends have shown that n-propanol and i-butanol give smaller octane increases than methanol or ethanol in leaded

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gasoline/alcohol blends. The antiknock qualities of nonleaded gasoline/alcohol blends have also been investigated. These investigations also indicate that alcohols in general are considerably more effective octane improvers in blends utilizing low octane gasoline components as compared to high octane gasolines. See, for example, Cox, Frank W., PHYSICAL PROPERTIES OF GASOLINE/ALCOHOL BLENDS, Bartlesville Energy Technology Center, Bartlesville, Oklahoma (1979).

It is also known that lower molecular weight aliphatic alcohols and gasoline when blended together form nonideal mixtures with respect to octane numbers. This nonideal behavior results in an additional benefit in that the actual increase in octane value of a gasoline/alcohol mixture is greater than that expected from the amount of alcohol added and the octane value of the gasoline taken separately. Consequently, those skilled in this art generally use the octane value, known as "blending octane value", to estimate the effect of alcohol on the gasoline base. Blending octane value is the arithmetic average of the research octane value and the motor octane value and is typically expressed as  $(R + M)/2$ . For example, depending upon the octane values of the base gasoline, methanol/gasoline blends have been reported to be 2 to 3 Motor Octane Number and as high as 16 Research Octane Number above the reported values for the base gasoline. In any event, such finished methanol/gasoline fuels normally are 1.5 to 3 octane points  $(R+M)/2$  higher than the base fuel itself. See for example, Eccleston, B.H. and Cox, F.W., PHYSICAL PROPERTIES OF GASOLINE/METHANOL MIXTURES, Bartlesville Energy Research Center, Bartlesville, Oklahoma (1977).

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Notwithstanding these antiknock benefits, methanol by itself is not widely used as a gasoline additive due to the number of serious technical and legal problems associated with its use. In the technical realm, the presence of even small amounts of water can cause serious operational problems. Methanol when used by itself (and to a lesser extent ethanol) tends to phase-separate from gasoline in the presence of water and/or when exposed to cold weather conditions. This tendency to phase-separate has been an obstacle to the use of such alcohols as octane enhancers and gasoline extenders. Further, methanol, particularly when it has phase-separated from gasoline, is known to have harmful corrosive tendencies to certain fuel delivery and engine components.

It is also known in the art that lower molecular weight alcohols when combined with gasoline increase front end volatility (Reid Vapor Pressure - RVP), depress or displace the initial fractions of the distillation curve which tend to increase evaporative emissions.

For these and other reasons, Section 211(f)(a) of the Clean Air Act, as amended (42 USC 7445), governs the usage and introduction of additives in unleaded gasolines and specifically provides that no fuel or fuel additive may be first introduced into commerce that is not "substantially similar" to any fuel or fuel additive used in the certification of any 1974 or later model year vehicle. In July 1981, EPA defined "substantially similar" to include fuels with up to 2.0 wt. percent oxygen. Ethers or alcohols (except methanol) are acceptable additives if they otherwise meet these oxygen limitations. Methanol can be used as a de-icer when used up to 0.3 volume percent or be used for this purpose up to 2.75 volume percent when introduced with an equal volume of butanol or a higher

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molecular weight alcohol. However, the fuel must conform to the characteristics of an unleaded gasoline as specified by ASTM D 439. This definition of "substantially similar" provides a general rule for the inclusion of oxygenates in unleaded gasolines. Methyl tertiary butyl ether (MTBE) qualifies under the general 2% oxygen rule. This is equivalent to about 11% MTBE by volume, depending on the specific gravity of the gasoline.

The Clean Air Act under Section 211(f)(4) provides that the EPA Administrator may waive the prohibition on new fuels or fuel additives. However, prior to granting a waiver the Administrator must determine if the application meets the burden of demonstrating that the new fuel or fuel additive will not cause the failure of an emission control system or an emission standard(s). Under this section of the Act, the Administrator has both denied and granted several waiver requests.

The EPA has denied all previous waiver requests involving MMT in unleaded gasoline. The EPA denied Ethyl Corporation's MMT waiver applications because Ethyl failed to demonstrate that MMT at its proposed concentration levels of 1/16, 1/32 and 1/64 gram per gallon of gasoline would not cause or ultimately cause improper hydrocarbon emissions. See generally Environmental Protection Agency RE Applications for MMT Waiver, Federal Register, Vol. 43, No. 181, Monday, September 18, 1978, and Ethyl Corp; Denial of Application for Fuel Waiver; Summary of Decision, Federal Register, Vol. 46, No. 230, Tuesday, Dec. 1, 1981.

The EPA has also denied several waiver requests for alcohol additives. However, on September 23, 1981, Anafuel Unlimited was granted a waiver for a proprietary fuel called "Petrocoal" (see generally the

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Petrocoal Waiver and Supporting Docket EN 81-8). "Petrocoal" is a mixture of methanol and certain four-carbon alcohols in unleaded gasoline in the presence of a proprietary corrosion inhibitor. The fuel can contain up to 12 volume percent methanol and up to 15 volume percent total alcohols. The ratio of methanol to four-carbon alcohols cannot exceed 6.5 to 1.0. The fuel must also meet ASTM D 439 specifications.

The EPA granted on November 16, 1981 a request by ARCO for a waiver for mixtures of methanol and gasoline-grade tertiary butyl alcohol "GTBA" (see generally the Oxinol Waiver and Supporting Docket EN-81-10). ARCO markets these mixtures under the name "Oxinol". The ratio of methanol to GTBA cannot exceed 1 to 1, and the concentration of oxygen in the finished fuel cannot exceed 3.5 weight percent. The 3.5% oxygen limit translates into about 9.6% by volume. The lower the methanol content, the greater the total alcohol volume allowable. At zero methanol content, the 3.5 weight percent oxygen is equivalent to about 16 volume percent GTBA.

In 1979, EPA granted a waiver for "gasohol", which contains 10 volume percent ethanol (see generally the Gasohol Waiver). However, the general rule of 2 weight percent oxygen would limit ethanol to about 5.5 volume percent. This left an "illegal" limit between the 5.5 and 10 percent levels. In 1982, EPA interpreted the "gasohol" waiver to include any amount up to 10 volume percent anhydrous ethanol in unleaded gasoline.

The above described legal limitations also follow from the physical properties of such alcohol gasoline compositions, e.g., vapor pressure, enleanment, initial distillation curve depression and evaporative emissions.

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For example, methanol is 50 percent by weight oxygen. This leads to a potential problem known in the art as "enleanment". Fuel introduction and delivery systems (e.g., fuel injection systems, carburetors) are designed and adjusted to provide a predetermined stoichiometric amount (ratio) of air to fuel, and hence the amount of oxygen to fuel. In fuel carburetors and in cars without oxygen sensing devices this predetermined stoichiometric ratio is calculated without regard for gasolines containing oxygen. If a gasoline contains excessive concentrations of oxygenated components such as methanol, the air (oxygen) to fuel ratio is significantly changed from the predetermined ratio. Signification deviations from the predetermined ratio causes poor ignition and combustion properties of the fuel. A high air (oxygen) to fuel ratio produced in this manner will cause the engine to run lean. If an engine's air (oxygen) to fuel ratio becomes too high or lean, the engine will fail to start and/or continue to run.

In effect enleanment sets a technical limit on the total amount of any oxygenated component such as alcohol that can be incorporated into a gasoline without making major modifications to most fuel introduction and delivery systems. Moreover, higher air (oxygen) to fuel ratios also may contribute to the production of certain environmentally harmful nitrogen oxides.

An attribute of enleanment which heretofore has not been distinguished by those skilled in the art is called "technical enleanment". Technical enleanment is that unexpected phenomena which exhibits symptoms of enleanment occurring when the total air (oxygen) content of the finished fuel is not stoichiometrically or chemically lean. Such behavior is very similar to enleanment and includes engine stalling, lack of power,

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poor combustion, difficult start-ups (especially warm start-ups) and other problems normally associated with alcohol/gasoline fuels and combustion/fuel systems which are known to be chemically or stoichiometrically lean. The difference between chemical or stoichiometric enleanment and technical enleanment is that traditional chemical or stoichiometric enleanment can be predicted from a chemical and/or stoichiometric basis, whereas technical enleanment is not predictable on the same basis.

As mentioned above, alcohols typically increase Reid vapor pressure, depress the initial fraction of the distillation curve, together tending to increase evaporative emissions. Typically, methanol at 5 to 10 volume percent concentrations increases the blended fuel's vapor pressure from 1.5 to 3.5 p.s.i. over the base fuel itself. This negative characteristic is known in the art as a nonideal positive vapor pressure increase, because heat methanol has a vapor pressure lower than that of the base gasoline to which it is blended. Similarly, other lower molecular weight alcohols tend to exhibit similar nonideal vapor pressure attributes.

Since the EPA has exclusive jurisdiction of unleaded gasoline additives, emissions are a major concern when incorporating alcohols into unleaded gasolines. Numerous studies on this subject, including prior EPA waiver applications for alcohol additives, exist in the literature. These studies generally show that evaporative emissions are related to front end volatility (RVP) and the volatility of the initial to midpoint distillation fraction (up to approximately 200°F). Further, these studies show that carbon monoxide emissions are reduced, and that nitrogen oxide emissions are generally unchanged. Hydrocarbon emissions from such fuels generally vary. For example,

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Appendix B of the EPA's Waiver for Petrocoal showed the fuel's hydrocarbon emissions to be unchanged, see Federal Register Vol. 46, No. 192, Monday, 10/5/81, Page 48978. However, in one of the more comprehensive studies on the subject prepared under the direction of the U.S. Energy Research and Development Administration, hydrocarbon emissions increased with the introduction of methanol. Hydrocarbon emissions increased further by increasing the methanol concentrations in the base gasoline. See J.R. Allsup, EXPERIMENTAL RESULTS USING METHANOL AND METHANOL/GASOLINE BLENDS AS AUTOMOTIVE ENGINE FUEL, Bartlesville Energy Research Center, Bartlesville, Oklahoma (1977).

The use of aromatic hydrocarbons particularly in streams or fractions thereof in the range of C<sub>8</sub> - C<sub>25</sub> and subparts thereof, have heretofore been generally precluded from accepted usage in normal boiling range gasolines due to their high boiling temperatures and potentially harmful emissions. The use of these aromatic materials have traditionally been used as refinery intermediates and as components in gas oils, fuel oils, distillates and the like. Some of these aromatic hydrocarbons, for example, are recycle oils (cycle oils) from the catalytic cracker which are utilized as components in diesel fuel oils. Light cycle oils, the lighter fraction of cycle oils, typically have low cetane numbers but high octane numbers. The low cetane numbers make these fuels less attractive for diesel fuel, but their boiling temperatures and other attributes precludes their usage in gasolines.

Therefore, in view of the federally mandated ban on methyl cyclopentadienyl manganese tricarbonyls (MMT), the phase-out of leaded gasolines, the desirability of using aromatic hydrocarbons as substituent high octane

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05 components in gasoline, and in view of the above noted technical and legal problems associated with gasoline/alcohol blends, there now exists a very pressing need to find new families of environmentally safe antiknock agents and/or learn to use known antiknock agents in ways which are technically and environmentally acceptable. Applicants believe that the latter course holds the best immediate promise.

SUMMARY OF THE INVENTION

10 Applicants believe that the unacceptable hydrocarbon emissions and other pollution problems associated with the use of cyclomatic manganese tricarbonyls such as MMT are directly traceable to the associative build-up of unoxidized or partially  
15 oxidized hydrocarbons and oxides of manganese (believed to be " $Mn_3O_4$ "). The oxide of manganese is the oxidation product of the cyclomatic manganese tricarbonyls. Although the exact chemical mechanism of this hydrocarbon/ $Mn_3O_4$  build-up is not fully  
20 understood, Applicants believe that it begins with the formation of a hydrocarbon gum material ("HGM") comprised chiefly of unoxidized or partially oxidized hydrocarbons and  $Mn_3O_4$ . It is believed that once formed, the HGM tends to attract other unoxidized  
25 or partially oxidized hydrocarbons and  $Mn_3O_4$  which together tend to plug catalysts, foul spark plugs and form combustion chamber deposits. It is also believed, especially when the quantities of MMT are in excess of about 1/16 grams per gallon, that the  
30 presence of HGM causes a certain type of  $Mn_3O_4$  deposit in the catalytic converter system which ultimately causes it to plug.

35 Applicants have discovered that an unexpected beneficial chemical reaction(s) occurs when organomanganese containing unleaded gasolines are

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combined with Applicant's defined ingredients such that the resultant novel fuel composition can be made to meet current federal hydrocarbon emission standards while correcting the other negative phenomena normally associated with alcohol blends, namely technical enleanment, increased RVP, initial and mid-range distillation depression, high end boiling point temperatures and the resulting increase of harmful emissions. This novel fuel composition can become eligible for EPA Waivers of the type noted above which heretofore have been denied due to potential catalyst plugging and excessive hydrocarbon and other harmful emissions. The beneficial effect of this novel fuel is achieved by the use of certain well-defined proportions of C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols, well-defined proportions of cyclopentadienyl manganese tricarbonyl antiknock agents and aromatic hydrocarbons together with unleaded gasoline bases.

Applicants have further discovered that usage of the well-defined proportions of cyclopentadienyl manganese tricarbonyl antiknock agents in unleaded gasoline bases together with the well-defined proportions of C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols and aromatic hydrocarbons in a manner more fully described below, unexpectedly alleviates and corrects the phenomena of increased hydrocarbon emissions, technical enleanment, increased RVP, initial and mid-range distillation depression, high end boiling point temperatures and resultant increases in emissions.

No blending stabilizers are necessarily required when these three ingredient categories are combined in applicants' defined proportions. However, certain cosolvents may be added when desirable with aromatic hydrocarbons to control end boiling point temperatures and when methanol is used to control the phase stability of the fuel composition.

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DESCRIPTION OF THE DRAWINGS

Figure 1 plots temperature versus percentage of distillate recovered for various fuel blends and graphically depicts the improved distillation characteristics of Applicant's novel fuel composition.

Figure 2 plots hydrocarbon emissions (gr/mi) versus manganese concentration (gr/gal.) in various fuel blends.

DETAILED DESCRIPTION OF THE INVENTION

### 1. Defined Proportions of the Ingredients

The defined operational range of proportions over which the gasoline bases, the C<sub>1</sub> to C<sub>6</sub> aliphatic alcohol component, the cyclopentadienyl manganese tricarbonyl component and the aromatic hydrocarbon component may be employed to reduce hydrocarbon and evaporative emissions, correct technical enleanment and improve RVP, control initial and mid-range distillation depression and control end boiling point temperatures is:

#### TABLE OF INGREDIENT RANGES

Unleaded base	70-97	62-94	53-91	40-87	35-78
Gasoline (Vol.%)					

C <sub>1</sub> to C <sub>6</sub> alipha-					
1 6					

tic alcohols*	up to 5	5-8	8-12	12-20	20-30
(vol.%)					

0 % by weight**	up to 2.4	1.0-3.8	1.2-5.7	1.9-9.5	3.1-14.2
2					

Cyclopentadienyl					
manganese tri-	up to 1	up to 5	up to 3	up to 7	up to 1
carbonyl (grams	2	8	4	8	
of manganese/gallon					
fuel product)					

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Aromatic Hydro- up to 25 up to 30 up to 40 up to 45  
Carbons (Vol.%)

\*including the total volume of cosolvents, if any.

\*\*including the oxygen content of cosolvents, if any.

05        Generally, within these ranges, the higher the  
total concentration of the lower boiling point  
alcohols (particularly methanol, ethanol and propanol  
in order of their preference) the higher the preferred  
concentrations of manganese. However, the beneficial  
10       hydrocarbon emission and other ameliorative effects of  
this invention do not generally begin to occur until  
approximately 1.0% oxygen by weight of the C<sub>1</sub> to  
C<sub>6</sub> alcohol component is introduced into the fuel  
composition.

15       When methanol is used as the sole aliphatic  
alcohol without the benefit of any cosolvent(s) it  
should be limited to a concentration of about 5 volume  
percent or less of the fuel composition.

20       However, in most cases when methanol is employed  
in concentrations ranging from about 1 to about 24  
volume percent of the fuel composition, a cosolvent or  
group of cosolvents, selected from the group  
consisting of C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols,  
C<sub>3</sub> to C<sub>12</sub> ketones and/or C<sub>2</sub> to C<sub>12</sub>  
25       ethers in concentrations from about 1 to about 20  
volume percent should also be employed. The combined  
methanol and cosolvent concentration should, however,  
not exceed 30 volume percent of the entire fuel  
composition. When the cosolvent alcohol(s) is  
30       selected from the group consisting of C<sub>2</sub> to C<sub>8</sub>  
aliphatic alcohols, the preferred aliphatic alcohol is  
a saturated aliphatic alcohol(s).

35       In the practice of this invention one or more  
C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols, preferably,  
C<sub>1</sub> to C<sub>6</sub> saturated aliphatic alcohols, must be

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employed in the fuel composition. The alcohol component maybe any individual alcohol or any combination or mixture thereof. Mixed alcohol combinations may be desirable for enhancing blending octane values and controlling RVP increases. It is contemplated in the practice of this invention that mixed alcohols produced from the modification of known methanol catalysts, use of alkali metal oxide catalysts, use of rhodium catalysts, isosynthesis using alkalized ThO<sub>2</sub> catalysts, use of modified Fischer-Tropsch catalysts, modified turgi catalysts, and/or produced from certain isomerization/dehydrogenation processes, olefinic/hydration processes, "OXO" processes and the like, are acceptable.

Alcohol mixtures, generally having methanol, ethanol, propanols, butanols, pentanols and hexanols in the composition; which by weight percent of the composition decline as the individual molecular weight of the alcohol increases, are desirable. An example of a mixed alcohol composition wherein the lower molecular weight alcohols have a higher relative proportion of the composition by volume percent than do the higher molecular alcohols include: methanol at approximately 50 weight percent of the alcohol component, ethanol at approximately 25 weight percent, propanols at approximately 13 weight percent, butanols at approximately 6 weight percent, pentanols at approximately 3 weight percent, with hexanols and other higher alcohols generally representing the balance of the alcohol component.

Another example of a desirable alcohol mixture would include a composition wherein the higher molecular weight alcohols have higher relative proportions by volume percent of the composition than do the lower molecular weight alcohols. Still another

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example would include a mixed alcohol composition wherein similar proportions of each alcohol exist by volume percent in the composition. Mixed alcohol compositions generally include methanol to higher alcohol ratios generally varying from 4:1 to 1:4 weight percent of the alcohol compositions. Those other combinations of alcohol mixtures which positively effect RVP, octane, distillation characteristics, end boiling point temperatures, and/or emissions are particularly desirable.

Suitable alcohols for use include methanol, ethanol, N-propanol, isopropanol, N-butanol, secondary-butanol, isobutanol, tertiary butanol, pentanols, hexanols and the like. As noted in the Table of Ingredient Ranges, aliphatic alcohols in ranges from up to about 30.0% by volume with about up to 14.2% oxygen by weight give excellent hydrocarbon emission results when used in unleaded gasolines. The composition should have at least 0.001 grams manganese and generally no more than one gram manganese of a cyclomatic manganese tricarbonyl compound per gallon. Preferably, the alcohol employed should be anhydrous, but alcohols containing small amounts of water can also be used. Within the preferred concentration range most of the C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols are completely miscible with petroleum hydrocarbons and it is preferred that such alcohols be used in amounts within their solubility limits. However, if desirable, an amount of alcohol in excess of its solubility can be incorporated in the fuel by such means, as for example, by use of mutual solvents.

An acceptable cyclomatic manganese tricarbonyl concentration range is from about 0.001 to about 1.0 grams manganese per gallon of fuel composition. A more acceptable range is from about 1/64 to about 1/2 grams manganese per gallon of composition. A more

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desirable and preferred range is from about 1/64 to about 1/4 grams manganese per gallon of composition. An even more preferred range is from about 1/64 to about 1/8 grams manganese per gallon of composition. The preferred cyclomatic manganese tricarbonyl used in the composition is methyl cyclopentadienyl manganese tricarbonyl (MMT).

The acceptable oxygen by weight in the fuel composition is up to about 14.2 weight percent. A more desirable range would be from about 1.0 to about 8.0 weight percent. A preferred range would be from about 1.0 to about 5.0 weight percent. The most preferred range is from about 2.0 to about 3.5 weight percent of the fuel composition.

An acceptable range of aromatic hydrocarbons is up to about 45 percent. A desirable range is from about 1.0 to about 20 volume percent of the composition. A preferred range would be from about 1.0 to about 10.0 volume percent of the composition. A more preferred range would be from about 1.0 to about 5.0 volume percent of the composition.

An acceptable boiling range of the aromatic hydrocarbons including streams or fractions containing aromatic hydrocarbons is up to about 700°F. A more acceptable range is from about 200°F to about 550°F. A preferred range is from about 200°F to about 500°F, and a more preferred range is from 250°F to about 450°F. Preferred end point boiling ranges are from approximately 400°F to 550°F.

It is contemplated that in order to maximize the benefits of this invention that the fuel composition is to be constructed within the scope of the Table of Ingredient Ranges above.

Desirable individual alcohol compositions would contain from about up to about 5 volume percent methanol, or up to about 15 volume percent ethanol, or

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up to about 18 volume percent isopropanol, or up to about 18 volume percent normal propanol, or up to about 20 volume percent tertiary butanol, or up to about 20 volume percent secondary butanol, or up to about 20 volume percent isobutanol, or up to about 20 volume percent normal butanol, or up to about 25 volume percent pentanols, or up to about 30 volume percent hexanols and aromatic hydrocarbons from up to about 20 volume percent together with MMT as the cyclopentadienyl manganese in a concentration of up to about 1/4 gram of manganese per gallon of fuel composition. A more preferred composition would contain aromatic hydrocarbons from about 1.0 to about 10 volume percent and a MMT concentration from about 1/64 to about 1/8 grams of manganese per gallon of fuel composition.

A desirable alcohol/gasoline fuel composition includes a C<sub>1</sub> - C<sub>6</sub> alcohol component from about 2 to 30 volume percent, plus about 1/64 to 1 gram manganese of MMT per gallon of the composition with about 1 to about 45 volume percent aromatic hydrocarbons together with unleaded gasoline. A more desirable composition would contain aromatic hydrocarbons from about 1 to about 20 volume percent together with MMT from about 1/64 to 1/4 gram manganese of MMT per gallon of the composition.

A desirable alcohol (cosolvent)/gasoline fuel composition includes a C<sub>1</sub> - C<sub>6</sub> alcohol component from about 2 to 25 volume percent of the composition plus a cosolvent or group of cosolvents selected from the group consisting of C<sub>2</sub> - C<sub>12</sub> aliphatic alcohols, C<sub>3</sub> - C<sub>12</sub> ketones and/or C<sub>2</sub> to C<sub>12</sub> ethers in concentrations from about 1 to 20 volume percent, so that the combined alcohol and cosolvent concentration in the composition is not more than 30 volume percent. This fuel composition

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would be combined with about 1/64 to 1 gram manganese of MMT per gallon of the composition with about 1 to about 40 volume percent aromatic hydrocarbons in the composition together with an unleaded gasoline base.

05 A more desirable composition would contain aromatic hydrocarbons from about 1 to about 20 volume percent together with MMT from about 1/64 to about 1/4 grams manganese per gallon of composition. A preferred composition would contain aromatic hydrocarbons from  
10 about 1 to 10 volume percent together with MMT from about 1/64 to 1/8 grams manganese per gallon of the composition. An even more preferred composition would contain aromatic hydrocarbons in a concentration range up to about 6 volume percent of the composition.

15 Another desirable fuel composition contains methanol from about 1 to about 15 volume percent of the composition, C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols, C<sub>2</sub> - C<sub>12</sub> ethers and/or C<sub>3</sub> - C<sub>12</sub> ketones in concentration from about 1 to about 15 volume  
20 percent of the composition and a MMT concentration from about 1/64 to about 1/2 gram of manganese per gallon of fuel composition together with about 1.0 to about 20 volume percent aromatic hydrocarbons. A preferred MMT concentration would be from about 1/64  
25 to about 1/4 grams manganese per gallon of the composition together with about 1.0 to about 10 volume percent aromatic hydrocarbons. A more preferred MMT concentration would be from about 1/64 to 1/8 grams manganese per gallon of the fuel composition with  
30 about 1.0 to about 5 volume percent aromatic hydrocarbons.

A preferred fuel composition contains methanol from about 1 percent to about 9 volume percent of the composition, C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols in  
35 concentrations from about 1 to about 10 volume percent of the composition, a MMT concentration from about

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1/64 to about 1/4 gram manganese per gallon of fuel composition with aromatic hydrocarbons from about 1.0 to about 20 volume percent and a more preferred MMT concentration from about 1/32 to 1/8 gram per gallons with aromatic hydrocarbons from about 1.0 to about 10 volume percent of the fuel composition.

A more preferred fuel composition contains methanol from about 2 to about 6 volume percent with C<sub>2</sub> to C<sub>12</sub> saturated aliphatic alcohols in concentration from about 1 percent to about 10 volume percent of the composition and a MMT concentration from about 1/64 to about 1/4 gram manganese per gallon of fuel composition together with about 1.0 to about 20 percent aromatic hydrocarbons in the composition and an even more preferred MMT concentration is from about 1/64 to 1/8 gram per gallon together with about 1.0 to about 10 volume percent aromatic hydrocarbons in the composition.

Another highly preferred fuel composition would contain methanol from about 2 to 6 volume percent with C<sub>4</sub> to C<sub>12</sub> saturated aliphatic alcohols in concentrations from about 1 percent to about 10 volume percent of the composition, particularly those having boiling points higher than tertiary butanol and a MMT concentration from about 1/64 to about 1/4 grams manganese per gallon of fuel composition together with about 1.0 to about 20 percent aromatic hydrocarbons in the composition. A more preferred MMT concentration would be from about 1/64 to 1/8 gram per gallon together with about 1.0 to about 10 volume percent aromatic hydrocarbons in the composition.

## 2. The Use of Aromatic Hydrocarbons

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Aromatic hydrocarbons often are the resultant product of the reformer, Fluid Catalyst Cracker Unit (FCC), Riser Cracker Unit or Coker Unit using naphthas, gas oils, resid, coal liquids, shale oils, asphalt and/or other similar feed stocks. Aromatic hydrocarbons may also be the product of other reaction processing units within a petrochemical complex or refinery. These aromatic hydrocarbons may be streams themselves. Nonlimiting examples of Applicant's contemplated aromatic hydrocarbons include reformates, raffinates, platformates, alkalates, naphthas, distillates, isomerates, polymerates, light cycle oils, coal liquids, biomass liquids, wood liquids and the like.

These aromatic hydrocarbons or aromatic based hydrocarbon streams normally boil in ranges which include temperatures inside and/or outside normal gasoline boiling temperatures. They often are components of streams which themselves can not readily be added to gasoline or streams which can not be economically processed into gasoline for various reasons. Often these streams contain significant quantities of olefins and paraffins. Higher octane components are preferred, especially branched chain, condensed ring and iso-paraffins and olefins. In certain cases these streams are exclusive of aromatic hydrocarbons. As an example, light cycle oils which are generally known to be fluid catalytic cracker (FCC) recycle oils and which are produced by the FCC from heavy gas oils, have boiling ranges normally varying from about 300°F to about 650°F and in certain cases boiling at temperatures outside these ranges. Light cycle oils are generally recycled through the FCC to produce additional gasoline material until the economics of recycling diminish and they become a component of distillate, diesel fuel oils, or other fuels.

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Acceptable aromatic hydrocarbons are those having boiling ranges from approximately 200°F to 700°F and in certain cases boiling temperatures outside these ranges. Applicant's aromatic hydrocarbons, or streams or fractions containing aromatic hydrocarbons thereof are those with a carbon molecular content up to generally C-25, more preferred are those up to C-15, with the most preferred being those between C-5 to C-15. Typically, Applicant's aromatic hydrocarbons can be added to or processed into gasoline only at additional expense to the refiner because of the nature of the process stream itself. Often this additional expense is prohibitive. In many cases the additive cost of their recycling, distillation, coking, reforming, polymerization, isomerization, alkalation, cracking and the like preclude their economic usage in gasoline altogether. This phenomena may be associated with the particular hydrocarbon streams molecular characteristics or effluent hydrocarbon composition. In other cases aromatic hydrocarbons are not included in gasoline because of concerns of increased exhaust emissions.

Applicant has discovered that with the addition of MMT, C<sub>1</sub> to C<sub>6</sub> alcohols, aromatic hydrocarbons and as cases require the addition of cosolvents together with a normal boiling range gasoline base that there is an unexpected reduction in anticipated emissions as well as the end boiling point temperatures of the composition. Further, there is an improvement of RVP and the distillation characteristics of the fuel. See for example Figure 1 which presents the distillation curve of (1) a base gasoline, (2) an aromatic hydrocarbon, (3) the base gasoline at 95% by volume and the aromatic hydrocarbon at 5% by volume, and (4) the base gasoline at 85% by volume, aromatic hydrocarbon at 5% by volume and

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alcohols at 10% by volume. The alcohols used therein are methanol and pentanol in equal parts.

05 Note the unexpected reduction of the end boiling point of the alcohol based gasoline the with aromatic hydrocarbon. This unexpected end boiling point reduction of \_\_\_\_\_ allows the introduction of certain aromatic hydrocarbons or streams or fractions containing aromatic hydrocarbons into gasoline which heretofore would not have or could not have  
10 practically been included without additional processing and the like.

It is contemplated within the practice of this invention that by varying the molecular weight and concentration percentages of Applicant's ingredients together with varying and tailoring the aromatic  
15 hydrocarbons, their boiling ranges and the like, that different octane, RVP, distillation and end boiling point responses will be experienced. Obviously the compositional nature of the aromatic hydrocarbons will also influence their responses.  
20

It is also within the scope and practice of this invention to utilize different molecular weight cosolvents (especially of higher molecular weight) in varying combinations and concentrations together with  
25 aromatic hydrocarbons as a means of controlling RVP, initial and mid-range distillation depression, as well as end boiling point temperatures.

It appears that the defined use and combination of Applicant's alcohols (cosolvents) and MMT improves the  
30 fuel so that aromatic hydrocarbons and hydrocarbon streams containing aromatic hydrocarbons which normally would not have been added to or processed into gasoline now may become compatible for usage in normal boiling range gasolines. Certain aromatic  
35 hydrocarbons when used alone in gasolines, even at lower concentration levels tend to increase exhaust

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emissions and create driveability problems. However, the addition of Applicant's defined proportions of alcohol ingredients in combination with MMT tends to mitigate both the emission and driveability problems otherwise associated with the use of aromatic hydrocarbons in gasoline.

Figure 1 shows that the "uncorrected base fuel", (an alcohol gasoline composition without the balance of Applicant's MMT and aromatic hydrocarbon ingredients), has the expected initial and mid-range distillation fraction depression when compared to the base gasoline. Note that the "corrected fuel" (containing Applicant's defined ingredients) substantially improves the initial and mid-range distillation depression as well as improving the end boiling point characteristics of the "uncorrected base fuel with aromatic hydrocarbons" (without the benefit of Applicant's other ingredients).

The use of aromatic hydrocarbons in combination with Applicant's other ingredients also improves front end volatility (Reid Vapor Pressure).

Since the improvement of the initial and mid-range distillation characteristics and the improvement of RVP effectively improves evaporative emissions and controls technical enleanment, the addition of aromatic hydrocarbons in combination with Applicant's other ingredients clearly represents a significant departure from the current art understanding of various alcohol/gasoline blends and gasoline compositions in general.

In the practice of this invention most aromatic based hydrocarbon streams or fractions thereof are acceptable. However, generally acceptable aromatic hydrocarbons streams are those which have at least 10% by weight aromatic hydrocarbons, but those having an aromatic content in excess of 50% or more by weight

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are more preferred. It is also desirable that the hydrocarbon streams or fractions thereof have an octane  $(R + M)/2$  rating in excess of 50, a more preferred octane rating would be in excess of 70, an even more preferred octane rating would be in excess of 85 (generally, the higher the octane rating the better). In most cases, the initial lighter, lower boiling point hydrocarbon based fractions boiling between 200°F to 450°F are preferred over those fractions boiling between 200°F to 550°F over those fractions boiling from 200°F to 700°F.

In addition to using aromatic hydrocarbons which are typically found in normal boiling range gasolines it is also within the scope and teachings of this invention to utilize aromatic hydrocarbons streams or fractions thereof and/or any other aromatic based hydrocarbon streams or fractions thereof which would not normally be used in normal boiling range gasolines in significant quantities, if any. It is within the teachings and scope of this invention to substitute an individual aromatic hydrocarbon with other aromatic hydrocarbons, with aromatic hydrocarbon streams or fractions thereof, with aromatic based hydrocarbon streams or fractions thereof. Aromatic hydrocarbon substitution may also be made with acceptable non-aromatic hydrocarbon streams or fractions thereof. It is further within the scope and teachings of this invention that certain aromatic hydrocarbon based fractions which would have to be cut at lower temperatures in order to be included into gasoline, may now be cut at higher temperatures with a greater percentage of the stream being included into gasoline. Such streams or fractions thereof are within Applicant's teachings of aromatic hydrocarbons. It is further contemplated in the practice of this invention that aromatic hydrocarbon

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streams or fractions thereof may be the product of isomerization units, crude distillation units, cokers, vacuum distillation units, hydrocracking units, catalytic cracking units, riser cracking units, reforming units, alkylation units, polymerization units, hydrodesulfurization units, pyrolysis units, gasification units and the like, and/or produced from any combination of these units using crude oil, natural gasolines, natural gas, natural gas liquids, heavy gas oils, coal, coal liquids, shale oil, biomass, wood, lignate, peat moss, tar sands and the like, at a refinery, petrochemical complex and/or other production complex.

The volume percentages of aromatic hydrocarbons up to 45% as taught in the Table of Ingredient Ranges and elsewhere in this invention are in addition to the aromatic content percentage of the unleaded gasoline bases as taught in Section 6 below.

Applicant contemplates that it may be necessary in certain circumstances to tailor the boiling characters and the distillation characteristics of these aromatic hydrocarbon streams or fractions thereof. Tailoring, for example, may include cutting the aromatic hydrocarbon so that its ending boiling point would be between 400°F to about 550°F. This may be desirable in order to conform to Applicant's blended fuel with ASTM D 439 standards. In certain instances it may be desirable to separate one or more components within the aromatic based hydrocarbon stream from other components of the stream. Other tailoring would include mixing various noncut or cut aromatic hydrocarbon fractions together.

In the practice of this invention it is desirable to utilize aromatic based hydrocarbons, or streams or fractions thereof which are least likely to cause gumming. However, in those cases where gum formation

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is likely to occur it may be desirable to reduce the concentrations of gum forming hydrocarbons in the composition, increase usage of other solvent ingredients of this invention and/or use appropriate gum inhibitors, such as antioxidants, and/or other antigumming agents.

By correcting the displacement in the distillation curve as presented in Figure 1 with the inclusion of aromatic hydrocarbons, MMT, and C<sub>1</sub> to C<sub>6</sub> alcohols (cosolvents) in accordance with the Applicant's described construction and proportions, Applicant has discovered a control for T.E., RVP, initial distillation depression, evaporative and hydrocarbon emissions as well as a mechanism to reduce the end boiling temperatures of aromatic hydrocarbons. The combined usage of aromatic hydrocarbons, MMT and C<sub>1</sub> to C<sub>6</sub> alcohols (cosolvents) exhibits a particularly ameliorative and unexpected synergism.

Naturally, the various combinations, production processes, tailoring and the like, including the aromatic hydrocarbon compositions themselves as taught in this invention will not possess exactly identical effectiveness, and therefore will vary as individual circumstances dictate. The most advantageous concentration for each such compound will vary and depend to a large extent upon the particular alcohol(s), (cosolvent(s), aromatic hydrocarbon(s) and unleaded gasoline components used as well as their respective concentrations, and MMT concentrations.

With Applicant's invention, Applicants can effectively improve the end boiling point and emission characteristics of the fuel composition which would normally be expected by the addition of the contemplated aromatic hydrocarbon. Applicant's may also control distillation depression and increased RVP

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05 which would normally occur with the addition of lower molecular weight alcohols. Applicant also corrects the excessive hydrocarbon emissions occurring with the addition of MMT to unleaded gasoline. These attributes of Applicant's invention represent a very significant departure from the prior art and in view of the prior art literature is quite unexpected and novel.

### 3. Reduction of Hydrocarbons Emissions

10 Applicant has also discovered that those MMT concentrations that heretofore have been considered excessive for reasons associated with unacceptable engine out hydrocarbon (EOHC) emissions and catalyst plugging, when combined with the aliphatic alcohols,  
15 aromatic hydrocarbons and unleaded gasoline bases in accordance with Applicant's noted proportions and construction, tend to prevent unacceptable hydrocarbon emissions and prevent catalyst plugging. In view of the extensive prior art literature on the subject,  
20 this result is quite unexpected.

The beneficial hydrocarbon emission effects are best illustrated in Figure 2. Figure 2 illustrates the range of hydrocarbon emissions on the basis of engine out hydrocarbons (EOHC) improvement expected at  
25 5,000 miles using the defined proportions of C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols (cosolvents), MMT, aromatic hydrocarbons and unleaded base gasolines (the "Corrected Fuels"), over fuels just employing MMT concentrations, without the benefit of C<sub>1</sub> to  
30 C<sub>6</sub> aliphatic alcohols and aromatic hydrocarbons (the "Uncorrected Fuels"). The 5,000 mile mark reflects the critical point where the initial assent in hydrocarbon emissions is typically experienced in MMT containing nonleaded fuels. The effect of

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methanol and its associated cosolvents, including alcohols, ethers and ketones, are incorporated in Figure 2. Figure 2 illustrates the significant differences in the hydrocarbon emission behavior of pre-1980 standard model cars (manufactured for under 1.5 grams of hydrocarbon emission per mile standards) using the "Uncorrected Fuels" and "Corrected Fuels" formulated in accordance with Applicant's invention.

In an effort to minimize the effect of EOHC emissions and increase the anti-knock concentrations of MMT one should employ the maximum concentrations possible of C<sub>1</sub> to C<sub>3</sub> alcohols. The highest preference is given to methanol, the second to ethanol and the third to propanol.

The preferred cyclomatic manganese tricarbonyl used in our composition is methyl cyclopentadienyl manganese tricarbonyl (MMT) but the composition can contain a homologue or such other substituents as, for example, alkenyl, aralkyl, aralkenyl, cycloalkyl, cycloalkenyl, aryl and alkenyl groups. Illustrative, but nonlimiting examples of such substituted and unsubstituted cyclomatic manganese tricarbonyl antiknock compounds are: cyclopentadienyl manganese tricarbonyl; methylcyclopentadienyl manganese benzyleyclopentadienyl manganese tricarbonyl; 1,2-dipropyl 3-cyclohexylcyclopentadienyl manganese tricarbonyl; 1,2-diphenylcyclopentadienyl manganese tricarbonyl; 3-propenylidenyl manganese tricarbonyl; 2-tolyindenyl manganese tricarbonyl; fluorenyl manganese tricarbonyl; 2,3,4,7 - propylfluorenyl manganese tricarbonyl; 3-naphthylfluorenyl manganese tricarbonyl; 4,5,6,7 - tetrahydroindenyl manganese tricarbonyl; 3-ethenyl-4, 7-dihydroindenyl manganese tricarbonyl; 2-ethyl 3 (α-phenylethenyl) 4,5,6,7 tetrahydroindenyl manganese tricarbonyl; 3 - (α-cyclohexylethenyl) -4,7 - dihydroindenyl manganese

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tricarbonyl; 1,2,3,4,5,6,7,8 - octahydrofluorenyl manganese tricarbonyl and the like. Mixtures of such compounds can also be used. The above compounds can generally be prepared by methods which are known in the art. Representative preparative methods are described, for example, in U.S. Patents 2,819,416 and 2,818,417.

Since the oxidation product of the above methyl cyclomatic manganese tricarbonyls play a leading role in HGM build-up, it is desirable to use as little of the methyl cyclomatic manganese tricarbonyl compounds as is necessary in order to maximize the HGM inhibition benefits of the invention. As seen in the Table of Ingredient Concentrations, concentrations of the methyl cyclomatic manganese tricarbonyl compound concentrations (expressed as grams of manganese metal per gallon of the resulting fuel composition) as low as 1/64 grams manganese per gallon are sufficient in many cases. However, concentrations up to and including 1.0 grams manganese per gallon can be employed, but are less preferred. On occasion, amounts outside of the above-recited range can also be employed, but such concentrations tend to be less satisfactory.

In terms of economic costs versus octane benefits, concentrations of cyclomatic manganese tricarbonyl in the range of from about 1/64 grams to about 1/4 grams manganese/gallon give good results, and concentrations from 1/64 to 1/8 grams manganese/gallon give better results and are preferred. This invention also contemplates the use of other additives, such as gum and corrosion inhibitors, multipurpose additives and scavengers, made necessary or desirable to maintain fuel system cleanliness and control exhaust emissions due to the presence of alcohol, organo-manganese compounds and aromatic hydrocarbons in the fuel. The

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methods of incorporation of such additives into fuel blends are well known to the art.

05 The utilization of aromatic hydrocarbons, especially the heavier higher boiling fractions, tend to aggravate  $\text{no}_x$ , carbon monoxide and hydrocarbon emissions, as compared to the long term hydrocarbon emission problems associated with the continued usage of MMT. Although Applicant is not entirely sure of the operating mechanism of his invention he believes  
10 that during combustion, MMT acts as some form of catalyst while in the presence of Applicant's other ingredients, so that the combustion product employing Applicant's ingredients is more complete and clean, thereby reducing the emissions otherwise associated  
15 with the use of aromatic hydrocarbons and MMT. Accordingly, Applicant believes that there is some sort of a three way synergism between aromatic hydrocarbons, MMT and lower molecular alcohols which together in unleaded gasoline, controls the emissions  
20 of the resultant fuel composition.

#### 4. Using Cosolvents

When methanol is used as the aliphatic alcohol of choice, then a cosolvent should also be employed to insure phase stability of the fuel composition to the  
25 extent that the fuel composition containing methanol and approximately 500 parts per million water will not phase separate at  $15^\circ\text{F}$ , or the lowest probable temperature to which the fuel composition will be exposed. Generally speaking the methanol to cosolvent  
30 ratio should not exceed about 5 parts methanol to 1 part cosolvent depending upon the nature of the base fuel and the cosolvent(s) used. There does not appear to be any minimum ratio of methanol to cosolvent, except as required by economics or the desired

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performance characteristics of the fuel composition. In certain cases if the amount of methanol used is about 5 percent by volume or less of the fuel composition, cosolvents may not be required. However, it is good practice to use cosolvents whenever methanol is employed.

The cosolvent(s) can be selected from the group consisting of C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols, C<sub>3</sub> to C<sub>12</sub> ketones and/or C<sub>2</sub> to C<sub>12</sub> ethers. Within the scope of this invention it is contemplated that these cosolvents may also be used with any C<sub>1</sub> - C<sub>6</sub> aliphatic alcohol, especially in cases where corrosion, phase stability or vapor pressure become an issue. It is also within the scope and teaching of this invention to employ one or more alcohols, ketones or ethers within a particular class of cosolvents and/or to employ any one or more cosolvents classes of this invention simultaneously.

It is further contemplated, within the scope of this invention, in cases where vapor pressure and/or evaporative emissions are a concern, especially when C<sub>1</sub> to C<sub>3</sub> molecular weight alcohols are used individually or in combination, to employ C<sub>2</sub> to C<sub>7</sub> ethers individually or in combination with each other with or without other cosolvents.

It is also within the scope and practice of this invention to use mixed cosolvents, including mixed alcohols, ethers and/or ketones as cosolvents. It has been found that mixed cosolvent alcohols particularly those in the C<sub>2</sub> to C<sub>8</sub> range have a particularly ameliorative effect on both RVP and octane blending values.

In accordance with the discussion of cosolvents within this invention with regard to phase stability, the preferred cosolvent class rankings would be alcohols first, ketones second, and ethers last.

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Also, the higher the average boiling point of the cosolvents employed within a particular class, up to a C<sub>8</sub> cosolvent, the greater the preference. With cosolvents greater than C<sub>8</sub> the reference is reversed so that a C<sub>9</sub> cosolvent would be preferred over a C<sub>10</sub> cosolvent and so forth.

Within the sub-categories of the particular cosolvent class, after preference is given to the alcohol, ketone and ether ranking, and after preference is given to the average boiling point characteristics, then preference would be given the branched chain molecules over straight or cyclical chained molecules.

The alcohol cosolvents will have from two to twelve carbon atoms. The preferred cosolvent alcohols are saturates having high water tolerances and high boiling points. Representative alcohol cosolvents include ethanol, isopropanol, n-propanol, tertiary butanol, 2-butanol, isobutanol, n-butanol, pentanols, amyl alcohol, cyclohexanol, 2-ethylhexanol, furfuryl alcohol, iso amyl alcohol, methyl amyl alcohol, tetrahydrofurfuryl alcohol, hexanols, cyclohexanols, septanols, octanols and the like. The alcohol cosolvents, in reverse order of their preference, are propanols, butanols, pentanols, hexanols and the other higher boiling point alcohols. The more preferred alcohol cosolvents include isobutanol, n-butanol, pentanol and the other higher boiling point alcohols.

The ketones used as cosolvents in fuel compositions taught herein will have from three to about twelve carbon atoms. Lower alkenyl ketones are, however, slightly preferred. Representative lower alkenyl ketones would include diethyl ketone, methyl ethyl ketone, cyclohexanone, cyclopentanone, methyl isobutyl ketone, ethyl butyl ketone, butyl isobutyl ketone and ethyl propyl ketone and the like. Other

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ketones include acetone, diacetone alcohol, diisobutyl ketone, isophorone, methyl amyl ketone, methyl isamyl ketone, methyl propyl ketone and the like. A representative cyclic ketone would be ethyl phenyl ketone.

Representative ethers which can be used as cosolvents in fuel compositions taught herein will have from 2 to about 12 carbon atoms and would include the preferred methyl alkyl t-butyl ethers such as methyl tert-butyl ether, ethyl tertiary butyl ether, also preferred tertiary amyl methyl ether, dialkyl ether, isopropyl ether, diisopropyl ether, diethyl ether, ethyl n-butyl ether, ethylidenedimethyl ether, butyl ether, and ethylene glycol dibutyl ether and the like. The representative straight ethers which can be used in the fuel blends of this invention would include straight chain ethers such as those presented above, as well as cyclic ethers wherein the ether's oxygen molecule is in a ring with carbon atoms. For example, 4,4-dimethyl-1, 3-dioxane, tetrahydrofurans, such as, for example, 2-methyltetrahydrofuran, 2-ethyltetrahydrofuran, and 3-methyletetrahydrofuran may also find use in the present invention. The most preferred ether would be a branch chained ether. In order to be most advantageously employed, the above ethers should also be readily soluble, either directly or indirectly in gasoline.

Generally, the preferred methanol/cosolvent ratio will range from 0.2 to 3 parts methanol to 1 part cosolvent. Ratios from about 3 to 5 parts methanol to 1 part cosolvent are also preferred in certain circumstances. The ratio of methanol to cosolvent can exceed 5 to 1 or be less than 0.5 to 1. However methanol/cosolvent ratios outside these ranges are normally less desirable unless vapor pressure or technical enleanment are issues in the fuel

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In formulating the desired alcohol (cosolvent) and aromatic hydrocarbon components and determining the preferred ratio of alcohols to cosolvent(s) to aromatic hydrocarbon the following factors should be taken into consideration:

05

10

15

- (1) The base gasoline composition.
- (2) The distribution system to which the finished fuel will be exposed to.
- (3) The average age of the vehicular population consuming the fuel.
- (4) The fuel's propensity towards alcohol related technical enleanment, increased RVP, evaporative emissions and the like.
- (5) The fuel's effect on exhaust emissions.
- (6) The mid and end range temperature of the composition.

20

25

Generally the more desirable the base fuel composition as described hereafter, the less restrictive will be the formulation and construction of the C<sub>1</sub> to C<sub>6</sub> aliphatic alcohol and cosolvent components. The more desirable the base gasoline, the greater the permissible percentage oxygen by weight that can be in the finished fuel, the better the RVP response and initial and mid-range distillation characteristics. The more desirable the base gasoline the greater the flexibility in reducing or increasing the total percent alcohol cosolvents by volume in the finished gasoline.

30

35

For example, generally, the higher the aromatic content of the base gasoline (as discussed later) the higher the permissible methanol to cosolvent ratio, and the lower the required average boiling point of the alcohol/cosolvent component. Inversely, a less desirable base gasoline with lower percentages of aromatic components generally will require, for

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formulation. The methanol to cosolvent ratios will generally be higher when a higher boiling point aliphatic alcohol up to C8 is the cosolvent and lowest when ethanol is the cosolvent. In the same sense methanol to cosolvent ratios are higher with alcohols, than they are with ketones, than they are with ethers. That is to say, when a comparable higher boiling point or molecular weight alcohol, ketone or ether is compared, the highest ratio (within the general range of 3 to 5 parts methanol to 1 part cosolvent) is permissible when the cosolvent is an alcohol, the second highest ratio when the cosolvent is the ketone and the lowest ratio when the cosolvent is an ether.

For example, in comparing normal-butanol,  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$ ; diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ ; and methyl ethyl ketone  $\text{CH}_3\text{COCH}_2\text{CH}_3$ ; the preferred ratios might be 3 to 5 parts methanol to 1 part N-butanol, 1 to 2 parts methanol to 1 part methyl ethyl ketone, and 1 part methanol to 2 to 3 parts diethyl ether. Within each of these cosolvent groups, the methanol-cosolvent ratios should be at their highest when higher molecular weight cosolvent molecules (e.g., C<sub>4</sub> - C<sub>12</sub>) are used.

It is also within the scope and practice of this invention to utilize individual and/or different molecular weight cosolvent mixtures, higher alcohol mixtures (especially C<sub>4</sub> - C<sub>12</sub> in varying combinations and concentrations together with aromatic hydrocarbons as a means of controlling RVP, initial and mid-range distillation, depression, and end boiling point temperatures.

5. Formulating the C<sub>1</sub> - C<sub>6</sub>  
Alcohol (Cosolvent) and Aromatic  
Hydrocarbon Components

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example, a lower methanol to cosolvent ratio and a higher average boiling point alcohol and cosolvent components. This same low aromatic gasoline will limit the flexibility of reducing or increasing the total volume of the alcohol component. It is likely that the alcohol component as a percent of volume would be easier to increase than it would be to decrease.

It is known in the art that certain azetropic relationships aggravate the alcohol and cosolvent component configurations as well. Also, particular attention must be given to the characteristics of technical enleanment. Generally in gasolines with higher relative mid-range volatility and/or higher paraffinic content, the methanol to cosolvent ratios are lower, sometimes less than 1. In these cases the required average boiling point of the alcohol (cosolvent) component is normally higher, and the flexibility of either increasing or reducing the total alcohol (cosolvent) component is restricted. The permissible oxygen content is normally reduced and in some severe cases it should not exceed 2.5% by weight. In these base gasolines it is important to construct the alcohol (cosolvent) component so as to prevent any significant displacement of the lower and particularly the mid-range gasoline fractions during distillation. It is also desirable, as in the case of aromatic hydrocarbons, to construct the alcohols (cosolvents) volatility (distillation) in the composition to match the base gasoline's hydrocarbon volatility as closely as possible, especially in the initial and mid-range fraction areas.

In addition to considering the base gasoline to which the alcohol (cosolvent) component is added, consideration must also be given to the fuel distribution system to which the finished fuel will be exposed. The greater the likelihood of significant

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05 exposure to moisture, temperature variations and cold weather conditions, the more restrictive the alcohol (cosolvent) component construction and the greater the possible alcohol volume, the higher the average molecular weight of the alcohols, and the lower the permissible methanol to cosolvent ratio.

10 For example, a methanol to cosolvent ratio of 3 to 1 using isopropanol as the cosolvent, together with the alcohol component representing 7 percent by volume of the fuel, would normally be acceptable if the fuel were to be distributed in a dry system averaging 60°F. However, if it were anticipated that the fuel would be exposed to 20°F temperatures, or to greater concentrations of moisture or water, then certain  
15 adjustments would have to be made. One or more of the following adjustments would be required:

- 20 (a) The methanol to cosolvent ratios would be reduced to 2 to 1, or 1 to 1, increasing the average weight of the combined alcohol (cosolvents) component.
- (b) The cosolvent would be changed from isopropanol to a butanol or other higher boiling point alcohol(s).
- 25 (c) The volume of alcohol (including cosolvents) would be increased from 7 percent to 12 percent.

30 The age of the vehicular population which consumes the finished fuel also impacts the amount of oxygen which may be contained in the fuel. In the case of older automobiles the finished fuel may contain upwards to 5-7 percent total oxygen by weight. Those newer automobiles using 3-way catalysts which require more stringent air fuel ratios are limited to generally 4-5 percent total oxygen by weight. New vehicles

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containing oxygen sensing devices may use fuels containing upwards of 7 percent oxygen by weight. With the anticipated improvements of oxygen sensing devices in 1985 and future model years, the oxygen content of the finished fuel could approach 12 percent or more by weight.

Another element that must be considered when formulating the cosolvent component, is the cosolvent's effect with the aromatic hydrocarbon component on mid and end range distillation temperatures. Generally C<sub>2</sub> - C<sub>4</sub> alcohols (up to and including TBA), tend to reduce the mid-range distillation temperature. C<sub>4</sub> (higher than TBA) - C<sub>12</sub> alcohols tend to reduce temperatures beyond the mid-range. The inclusion of aromatic hydrocarbons into the fuel composition, on the other hand, raises end range temperatures and tends to compress the distillation curve with the effect of increasing mid-range temperatures. Therefore, effect must be given to the particular characteristics of the aromatic hydrocarbon component (i.e., boiling range, end boiling point and the like) when formulating the cosolvent component. Generally, the higher the end boiling point of the aromatic hydrocarbon component, the higher the average molecular weight of the cosolvent component. Obviously, effect must be given to the volume concentration of the aromatic hydrocarbon component in the fuel composition and the propensity of the aromatic hydrocarbon component to form binary and other types of azeotropes with the solvents, cosolvents, and the other substituents of the composition.

In formulating the aromatic hydrocarbon component of the composition, comparison must be made between their octane, RVP, emissions and distillation benefits versus the butane debit of utilizing certain lower molecular weight alcohols in the composition. Aromatic

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hydrocarbon use in gasoline will generally represent an attractive and economic utilization for the refinery. However, since the use of lower molecular weight alcohols generally increases RVP, the refinery must generally back out inexpensive butanes from the gasoline composition to reduce this RVP increase.

#### 6. Unleaded Base Gasoline Composition

Normally the gasoline to which this invention is applied is a lead fuel or substantially lead free gasoline. The gasoline bases in Applicants' fuel composition are conventional motor fuels boiling in the general range of about 70° to about 40°F. They include substantially all grades of unleaded gasoline presently being employed in spark ignition internal combustion engines. Generally they contain both straight runs and cracked stock, with or without alkylated hydrocarbons, reformed hydrocarbons and the like. Such gasolines can be prepared from saturated hydrocarbons, e.g., straight stocks, alkylation products and the like, with detergents, antioxidants, dispersants, metal deactivators, rust inhibitors, multi-functional additives, demulsifiers, fluidizer oils, anti-icing, combustion catalysts, corrosion and gum inhibitors, emulsifiers, surfactants, solvents and/or other similar or known additives. It is contemplated that in certain circumstances these additives may be included in concentrations above normal levels made necessary to accommodate the ingredients of Applicant's invention.

Generally, the base gasoline will be a blend of stocks obtained from several refinery processes. The final blend may also contain hydrocarbons made by other procedures such as alkylates made by the reaction of C<sub>4</sub> olefins and butanes using an acid catalyst such

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as sulfuric acid or hydrofluoric acid, and aromatics made from a reformer.

The olefins are generally formed by using such procedures as thermal cracking and catalytic cracking. Deyhydrogenation of paraffins to olefins can supplement the gaseous olefins occurring in the refinery to produce feed material for either polymerization or alkylation processes. The saturated gasoline components comprise paraffins and naphthenates. These saturates are obtained from: (1) virgin gasoline by distillation (straight run gasoline), (2) alkylation processes (alkylates), and (3) isomerization procedures (conversion of normal paraffins to branched chain paraffins of greater octane quality). Saturated gasoline components also occur in so-called natural gasolines. In addition to the foregoing, thermally cracked stocks, catalytically cracked stocks and catalytic reformates contain saturated components. Preferred gasoline bases are those having an octane rating of  $(R + M)/2$  ranging from 78-95. It is desirable to blend the gasoline base as contemplated in Applicant's invention so that the minimum aromatic content within a normal gasoline base, to which the balance of Applicant's ingredients are added to, is no less than 5% and preferably greater than 20%. This minimum aromatic content of the base gasoline may be generated and introduced into the gasoline as a compliment to or as a result of the process stream(s) or fractions thereof which are taught as necessary hydrocarbon ingredients of this invention. The gasoline base should have an olefinic content ranging from 1% to 30%, and a saturate hydrocarbon content ranging from about 40 to 80 volume percent.

The motor gasoline bases used in formulating the fuel blends of this invention generally are within the parameters of ASTM D-439 and have initial boiling

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points ranging from about 70°F to about 115°F and final boiling points ranging from about 380°F to about 440°F as measured by the standard ASTM distillation procedure (ASTM D-86). Intermediate gasoline fractions boil away at temperatures within these extremes.

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In terms of phase stability and water tolerance, desirable base gasoline compositions would include as many aromatics with C<sub>8</sub> or lower carbon molecules as possible in the circumstances. The ranking of aromatics in order of their preference would be: benzene, toluene, m-xylene, ethylbenzene, o-xylene, isopropylbenzene, N-propylbenzene and the like. After aromatics the next preferred gasoline component in terms of phase stability would be olefins. The ranking of preferred olefins in order of their preference would be; 2-methyl-2-butene, 2-methyl-1-butene, 1-pentene, and the like. However, from the standpoint of minimizing the high reactivity of olefins and their smog contributing tendencies, olefinic content must be closely watched. After olefins the least preferred gasoline component in terms of phase stability would be paraffins. The ranking of preferred paraffins in order of their preference would be; cyclopentane, N-pentane, 2,3-dimethylbutane, isohexane, 3-methylpentane and the like.

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In terms of phase stability, aromatics are generally preferred over olefins and olefins are preferred over paraffins. Within each specific class the lower molecular weight components are preferred over the higher molecular weight components.

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It is also desirable to utilize base gasolines having a low sulfur content as the oxides of sulfur tend to contribute to the irritating and choking characteristics of smog and other forms of atmospheric pollution. To the extent it is economically feasible, the base gasolines should contain not more than 0.1

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weight percent of sulfur in the form of conventional sulfur-containing impurities. Fuels in which the sulfur content is no more than about 0.02 weight percent are especially preferred for use in this invention.

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The gasoline bases of this invention can also contain other high octane organic blending agents. Nonlimiting examples include phenols (e.g., P-cresal, 2, 4 xylenal, 3-methoxyphenal), esters (e.g., isopropyl acetate, ethyl acrylate) oxides (e.g., 2-methylfuran), ketones (e.g., acetone, cyclopentanone), alcohols (furon, furfuryl), ethers (e.g., MTBE, TAME, dimethyl, diisopropyl), aldehydes and the like. See generally "Are There Substitutions For Lead Anti-Knocks?", Unzelman, G.H., Forster, E.J., and Burns, A.M., 36th Refining Mid-Year Meeting, American Petroleum Institute, San Francisco, California, May 14, 1971.

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The gasoline bases which this invention employs should be lead-free or substantially lead-free. However, the gasoline may contain antiknock quantities of other agents such as cyclopentadienyl nickel nitrosyl, N-methyl aniline, and the like. Antiknock promoters such as 2.4 pentanedione may also be included. The descriptive characteristics of one common base gasoline is given as example 2. Obviously many other standard and specialized gasolines can be used in Applicants' fuel blend.

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## EXAMPLE 2

CHARACTERISTICS OF BASE GASOLINE

	Reid Vapor Pressure, psi	7.2
	API Gravity @ 60F	64.4
05	ASTM Distillation Vol % Evaporate	Temp., F.
	IBP	86*
	5	115
	10	132
10	15	145
	20	157
	30	178
	40	197
	50	213
15	60	229
	70	250
	80	286
	90	353
	95	391
20	EP	428
	Lead Content, g/gal	0.005 (or less and preferably none)
	Sulfur Content, wt %	0.04
25	Research Octane Number	91.5
	Motor Octane Number	83.9
	Component	Vol.
	Paraffins	59.03
	Olefins	5.01
30	Naphthenes	6.63
	Aromatics	29.33
	Average Molecular Weight	101.3

The fuel composition of this invention can generally be prepared by adding the cyclopentadienyl manganese antiknock compound, the C<sub>1</sub> to C<sub>6</sub>

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alcohols and the cosolvents, if any, together with aromatic hydrocarbons together with the base gasoline with sufficient agitation to give a uniform composition to the finished fuel. It is essential in the practice of this invention only that the novel combination of additives, a cyclopentadienyl manganese tricarbonyl and the C<sub>1</sub> to C<sub>6</sub> alcohols and cosolvents, if any, along with aromatic hydrocarbons be present in the defined-proportions with unleaded gasoline bases immediately prior to vaporization and combustion of the fuel in the engine. Accordingly, it is within the scope of this invention to add the components of the composition as herein taught either separately in any sequence, or as a mixture with each other, so long as the foregoing requirement is met.

Those skilled in the art will appreciate that many variations and modifications of the invention disclosed herein may be made without departing from the spirit and scope thereof.

Thus having disclosed our invention, we claim:

CLAIMS

1. A fuel composition for spark ignition internal combustion engines comprising a mixture of:

05           a nonleaded gasoline base comprised of hydrocarbons boiling within the gasoline range with said nonleaded gasoline base representing from about 35 to about 97 volume percent of the fuel composition;

10           a cyclopentadienyl manganese tricarbonyl antiknock compound having a manganese concentration up to about 1.0 gram of manganese per gallon of the fuel composition; and

15           a solvent or group of solvents, including mixtures thereof, selected from the group consisting of C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols in a concentration up to about 30 volume percent of the fuel composition; and  
20           an aromatic hydrocarbon or group of aromatic hydrocarbons representing up to about 45 volume percent of the fuel composition.

2. The fuel composition of claim 1 wherein the cyclopentadienyl manganese tricarbonyl is MMT having a manganese concentration up to about 1/2 gram per gallon of the fuel composition.

3. The fuel composition of claim 1 wherein the cyclopentadienyl manganese tricarbonyl is MMT having a manganese concentration from about 1/64 to about 1/4 gram per gallon of the fuel composition.

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4. The fuel composition of claim 1 wherein the MMT concentration is from about 1/64 to about 1/8 grams manganese per gallon of the fuel composition.

5. The fuel composition of claim 1 wherein the aromatic hydrocarbon component consists of hydrocarbons within a range of C<sub>5</sub> to C<sub>25</sub>, or subpart therein.

6. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is an aromatic based hydrocarbon process stream or fraction thereof.

7. The fuel composition of claim 1 wherein the aromatic hydrocarbon component consists of hydrocarbons up to about C<sub>15</sub>.

8. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is at least 20% by weight aromatic hydrocarbons.

9. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is at least 50% by weight aromatic hydrocarbon.

10. The fuel composition of claim 1 wherein the aromatic hydrocarbon component has an octane rating  $(R + M)/2$  in excess of 50.

11. The fuel composition of claim 1 wherein the aromatic hydrocarbon component has an octane rating  $(R + M)/2$  in excess of 70.

12. The fuel composition of claim 1 wherein the aromatic hydrocarbon component boils within the range of 200°F to 700°F, or subpart therein.

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13. The fuel composition of claim 1 wherein the aromatic hydrocarbon component boils within the range of 250°F to 550°F, or subpart therein.

14. The fuel composition of claim 1 wherein the concentration of aromatic hydrocarbon is up to about 20 volume percent of the composition.

15. The fuel composition of claim 1 wherein the concentration of aromatic hydrocarbon is from 1.0 to about 10 volume percent of the fuel composition.

16. The fuel composition of claim 1 wherein the concentration of aromatic hydrocarbon is up to about 6 volume percent of the fuel composition.

17. The fuel composition of claim 1 wherein the aromatic hydrocarbon is highly aromatic and has an end boiling point from about 400°F to about 550°F.

18. A composition of claim 1 wherein the unleaded gasoline base has an  $(R + M)/2$  octane rating ranging from about 78 to about 95.

19. The fuel composition of claim 1 wherein the solvent is methanol in a concentration up to about 5 volume percent.

20. The fuel composition of claim 1 wherein the solvent is ethanol in a concentration up to about 15 volume percent.

21. The fuel composition of claim 1 wherein the solvent is isopropanol in a concentration up to about 18 volume percent.

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22. The fuel composition of claim 1 wherein the solvent is normal propanol in a concentration up to about 18 volume percent.

23. The fuel composition of claim 1 wherein the solvent is tertiary butanol in a concentration up to about 20 volume percent.

24. The fuel composition of claim 1 wherein the solvent is secondary butanol in a concentration up to about 20 volume percent.

25. The fuel composition of claim 1 wherein the solvent is isobutanol in a concentration up to about 20 volume percent.

26. The fuel composition of claim 1 wherein the solvent is normal butanol in a concentration up to about 20 volume percent.

27. The fuel composition of claim 1 wherein the solvent is pentanol in a concentration up to about 25 volume percent.

28. The fuel composition of claim 1 wherein the solvent is hexanol in a concentration up to about 30 volume percent.

29. A fuel composition of claim 1 wherein the solvent or group of solvents are C<sub>1</sub> to C<sub>6</sub> alcohols, individually, or in combination with each other, such that their total concentration would range up to about 30 volume percent of the composition.

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05 30. A fuel composition of claim 1 wherein the solvent or group of solvents consisting of C<sub>1</sub> to C<sub>6</sub> aliphatic alcohols exist in a concentration from about 2 to about 24 volume percent, together with a  
10 cosolvent or group of cosolvents, including mixtures thereof, consisting of C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols, C<sub>2</sub> to C<sub>12</sub> ethers and/or C<sub>3</sub> to C<sub>12</sub> ketones in a concentration from about 1 to about 20 volume percent of the fuel composition, so  
15 long as the combined total solvent and cosolvent concentration in the fuel composition does not exceed 30 volume percent.

31. A fuel composition for spark ignited internal combustion engines comprising a mixture of:

05 a nonleaded gasoline base comprised of hydrocarbons boiling within the gasoline range with said nonleaded gasoline base representing from about 70 to 98 volume percent of the fuel composition;

10 a cyclopentadienyl manganese tricarbonyl antiknock compound having a manganese concentration from up to about 1.0 gram of manganese per gallon of the fuel composition;

methanol in a concentration up to about 24 volume percent of the fuel composition; and

15 a cosolvent, or group of cosolvents, including mixtures thereof, selected from the group consisting of C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols, C<sub>3</sub> to C<sub>12</sub> ketones and/or C<sub>2</sub> to C<sub>12</sub> ethers in a concentration from up to about 20 volume percent of the  
20 concentration such that the total volume of methanol and cosolvent(s) together shall not exceed 30 volume percent of the fuel composition; and

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an aromatic hydrocarbon, group of aromatic based hydrocarbons, streams or fractions thereof representing up to about 45 volume percent of the fuel composition.

32. The fuel composition of claim 1 wherein the aromatic hydrocarbon component consists of hydrocarbons within a range of C<sub>6</sub> to C<sub>25</sub>, or subpart therein.

33. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is an aromatic based hydrocarbon process stream or fraction thereof.

34. The fuel composition of claim 1 wherein the aromatic hydrocarbon component consists of hydrocarbons up to C<sub>15</sub>.

35. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is at least 20% by weight aromatic hydrocarbons.

36. The fuel composition of claim 1 wherein the aromatic hydrocarbon component is at least 50% by weight aromatic hydrocarbons.

37. The fuel composition of claim 1 wherein the aromatic hydrocarbon component has an octane rating  $(R + M)/2$  in excess of 50.

38. The fuel composition of claim 1 wherein the aromatic hydrocarbon component has an octane rating  $(R + M)/2$  in excess of 70.

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39. The fuel composition of claim 1 wherein the aromatic hydrocarbon component boils within the range of 200°F to 700°F, or subpart therein.

40. The fuel composition of claim 1 wherein the aromatic hydrocarbon component boils within the range of 250°F to 550°F, or subpart therein.

41. A fuel composition of claim 31 wherein the concentration of aromatic hydrocarbon is from 1 to about 20 volume percent of the composition.

42. A fuel composition of claim 31 wherein the concentration of aromatic hydrocarbon is from 1 to about 10 volume percent of the fuel composition.

43. A fuel composition of claim 31 wherein the concentration of aromatic hydrocarbon is from 1 to about 5 volume percent of the fuel composition.

44. A fuel composition of claim 31 wherein the aromatic hydrocarbon is highly aromatic and has an end boiling point from about 400°F to about 550°F.

45. The composition of claim 31 wherein the MMT has a manganese concentration up to about 1/2 gram of manganese per gallon of fuel composition.

46. The composition of claim 31 wherein the MMT has a manganese concentration from about 1/64 to about 1/4 gram of manganese per gallon of fuel composition.

47. The fuel composition of claim 31 wherein the MMT has a manganese concentration from about 1/64 to about 1/8 gram of manganese per gallon of fuel composition.

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48. The fuel composition of claim 31 wherein the methanol has a concentration of about 1 to about 15 volume percent of the composition, the cosolvent is a C<sub>2</sub> to C<sub>12</sub> aliphatic alcohol and the cyclopentadienyl manganese tricarbonyls MMT having a manganese concentration of from about 1/64 to about 1/4 gram of manganese per gallon of fuel composition.

49. The fuel composition of claim 31 wherein the methanol has a concentration of about 1 to 9 volume percent of the fuel composition and the cosolvents are C<sub>2</sub> to C<sub>12</sub> aliphatic alcohols in concentration from about 1 to about 10 volume percent.

50. The fuel composition of claim 31 wherein the methanol has a concentration of about 2 to 6 volume percent of the fuel composition and the cosolvents are C<sub>3</sub> to C<sub>12</sub> aliphatic alcohols in concentration of about 1 to 10 volume percent of the fuel composition.

51. The fuel composition of claim 31 wherein the cosolvent is selected from the group of C<sub>4</sub> to C<sub>6</sub> saturated aliphatic alcohols in concentration of about 1 to about 10 volume percent of the fuel composition.

52. The fuel composition of claim 31 wherein the cosolvent(s) has an average boiling point higher than tertiary butanol in concentration of about 1 to about 10 volume percent of the fuel composition.

53. A composition of claim 31 wherein the nonleaded gasoline base has an (R + M)/2 octane rating ranging from about 79 to about 86.

54. The fuel composition of claim 31 wherein the methanol has a concentration of about 1 to about 15 volume percent, the cosolvent is selected from the group consisting of ethanol, normal propanol, isopropanol, normal butanol, isobutanol, secondary butanol, tertiary butanol, pentanol, hexanol, methyl tertiary butyl ether, ethyl tertiary butyl ether, tertiary amyl methyl ether, dialkyl ether, isopropyl ether, acetone, methyl ethyl ketone and methyl isobutyl ketone, individually or in combination, said cosolvent having a concentration from about 1 to about 15 volume percent and the cyclopentadienyl manganese tricarbonyl is MMT having a manganese concentration from about 1/64 to about 1/4 gram of manganese per gallon of fuel composition together with aromatic hydrocarbons having a concentration from about 1 to about 20 volume percent of the composition.

55. The fuel composition of claim 31 wherein the cosolvents are saturated aliphatic alcohols.

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ANY REFERENCE TO DRAWINGS SHALL BE CONSIDERED NON-EXISTENT  
(See Article 14(2))

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01757

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. <sup>4</sup> C10L 1/18, 1/30		
U.S. Cl. 44/53, 68		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>5</sup>		
Classification System	Classification Symbols	
U.S.	44/53, 56, 63, 68	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched <sup>6</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>*</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
Y	US, A, 3,030,195 (EWAN) 17 April 1962, col. 6. lines 25-31 and claims.	1-25
Y	US, A, 4,191,536 (NIEBYLSKI) 04 March 1980, col. 4, lines 10-30 and claims.	1-25
A	US, A, 3,153,901 (RIFKIN) 27 October 1964, See entire document.	1-25
A	US, A, 4,207,078 (SWEENEY ET AL) 10 June 1980, See entire document.	1-25
A	US, A, 4,437,436 (GRAIFF ET AL) 20 March 1984, See entire document.	1-25
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>3</sup>
15 October 1986		31 OCT 1986
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		Ellen McAvoy